19 March 2004

US402-1737003

HABS/AKN

Process for the Preparation of Methanol

UDL-298

DESCRIPTION

The present invention relates to conversion of synthesis gas into methanol at condensing conditions. In particular, the invention is a methanol preparation process being carried out in a slurry reactor, wherein condensed methanol product is utilised as suspension medium for a catalyst being active in the methanol synthesis reactions.

Synthesis gas is any gas composition comprising hydrogen and carbon dioxide and/or carbon monoxide being able to establish condensing conditions.
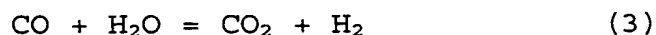
BACKGROUND OF INVENTION

Heterogeneous methanol synthesis is in today's practice carried out by reacting carbon oxides with hydrogen in the presence of copper-based catalysts according to the following equations:

$$3H_2 + CO_2 = CH_3OH + H_2O \qquad (1)$$
$$2H_2 + CO = CH_3OH \qquad (2)$$
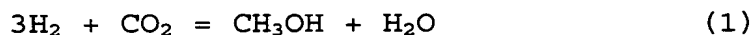
The methanol synthesis catalyst also catalyses the Water Gas Shift (WGS) reaction,

$$CO + H_2O = CO_2 + H_2 \qquad (3)$$

and

the Reverse Water Gas Shift (RWGS) reaction,

$$CO_2 + H_2 = CO + H_2O \qquad (4)$$
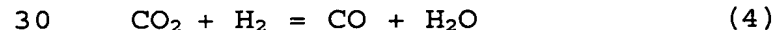
In large-scale methanol plants, the gas phase synthesis re-
actor is typically a cooled tubular reactor or a multistage
adiabatic reactor. The typical temperature range for metha-
nol synthesis is 200-300°C. Cooled reactors normally oper-
5   ate at approximately 250°C, whereas adiabatic reactors
typically operate between 220°C and 300°C. The reaction to
methanol is strongly exothermic, and efficient heat removal
is a problem. This limits the range of composition of the
feed gas that can be treated in a tubular reactor, for ex-
10   ample CO rich gases are very exothermic and difficult to
process. Inefficient heat removal leads to hot zones in the
reactor, and the catalyst may thus deactivate faster. A se-
rious problem is by-product formation being promoted at
high temperatures appearing particularly in the hot zones.
15   For example the production of ethanol, and methyl formate
increases at increasing temperatures. Alcohols, esters and
ketones are difficult to separate from methanol-water mix-
tures being withdrawn from the process due to the formation
of azeotropes.
20

With respect to pressure, the typical operating pressure in
methanol synthesis is within 50-100 bar. Cooled reactors
operate at a pressure of around 50 bar, whereas adiabatic
reactors generally operate at a higher pressure, typically
25   around 80 bar.

The synthesis gas used in methanol synthesis can be derived
from natural gas either by steam reforming of natural gas
or by autothermal reforming.
30

The conversion rate to methanol is determined by the ther-
modynamic equilibrium constant, which typically results in

process effluent concentrations being in the range between 4% and 10% in all cases with only a partial conversion of the carbon oxides. Thus, to obtain maximum use of the produced synthesis gas, a recycle of the unconverted gas is necessary. A high recycle ratio ensures high conversion. A high recycle flow through the reactor increases the compression cost. Before recycling, the effluent gas is cooled and separated from the liquid product. The effluent gas can be enriched in hydrogen by employing, for example, membrane separation. The enriched gas is recycled to the methanol reactor. The inert level, in particular methane is kept under control by purge.

Beside of the above mentioned tubular methanol reactor being conventionally employed in the industrial production of methanol use of slurry bed methanol reactors have also been suggested in the literature.

The original invention of the slurry reactor was made by Chem Systems and is described in US Patent No. 3,888,896. Herein a preparation process is described using an inert organic liquid such as pseudocumene as the slurry medium.

A series of patents from Air Products (US Patent Nos. 4,628,066, 4,766,154, 4,910,277, 5,179,129 and 5,284,878) describe the application of a slurry reactor for methanol synthesis. These applications are characterised by the suspension of the methanol catalyst in an inert liquid, typically a high-molecular-weight hydrocarbon. Only partial conversion of methanol is considered here, as the reaction conditions are given as 30-100 bar and 210-250°C.
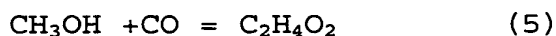
The finely divided catalyst must be separated from the liquid product. U.S. Patent No. 5,520,890 by Den Norske Stats Oljeselskap A.S. describes an apparatus for solid-liquid slurry treatment. The process described in this patent provides a solution for the separation of fine catalyst particles from the liquid by operation in tubes including filtrate zones.

JP Patent No. 57126434 discloses a methanol preparation method from CO and/or CO_2 in the presence of a water-soluble basic substance where water is used as slurry medium.

A completely different approach to methanol synthesis from alkyl formates was first described by J.A. Christiansen in US Patent No. 1,302,011. This approach is also described in US Patent No. 5,384,335 and consists of two distinct steps:

First step:
Carbonylation of methanol to methyl formate, $HCOOCH_3$ (= $C_2H_4O_2$), in a basic medium e.g.
$$CH_3OH + CO = C_2H_4O_2 \qquad (5)$$
Second step:
Reduction of methyl formate to methanol on a Cu-based catalyst
$$C_2H_4O_2 + 2H_2 = 2CH_3OH \qquad (6)$$
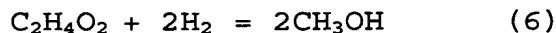
Various solvents are described including the use of methanol as a solvent. The conditions under which the above reactions take place differ significantly from the conditions applied in industrial methanol synthesis. Reaction 5 requires a temperature much lower than 200°C, whereas reac-

tion 6 is preferably carried out at much higher tempera-
tures. In some processes the reactions are actually carried
out in separate reaction vessels.

5   The most important difference between the above process and
the industrial methanol synthesis is the role of CO_2. In
the above process CO_2 acts as a poison for reaction 5,
whereas in the heterogeneous synthesis of methanol (reac-
tion 1) CO_2 is a necessary reactant. H_2O also acts as a
10   poison in the above process.

A conversion not limited by the thermodynamic equilibrium
can be obtained in the case of a methanol product removal
under synthesis. US Patent No. 5,262,443 to Haldor Topsoe
15   A/S describes such a process where methanol synthesis is
carried out under condensing conditions in a fixed bed in a
cooled tubular reactor. Methanol condensing conditions in-
clude a temperature below the critical temperature of
methanol, i.e. 240°C. In addition, the methanol partial
20   pressure calculated from the gas phase equilibrium constant
is larger than the boiling pressure of methanol at the ac-
tual temperature. The process is most conveniently carried
out with a stoichiometric synthesis gas being enriched in
CO.

25

The removal of heat in the tubular reactor disclosed in the
later patent and in tubular methanol reactors in general is
one of the key problems of such a process. The most serious
problem when employing fixed catalyst bed methanol reactors
30   is formation of by-products being formed in hot zones of
the bed caused by the highly exothermic nature of the
methanol reactions in the catalyst bed.

In contrast to the above discussed prior art, the present
invention is a preparation method for methanol at condens-
ing reaction conditions wherein the methanol catalyst is
suspended in methanol and water, and wherein the product

5   being formed on the suspended catalyst (primarily methanol
and water) continuously condenses and being absorbed in the
suspension and thus makes up the suspension medium for the
methanol catalyst.

10   When carrying out the methanol reactions in a catalyst sus-
pension heat being produced during the reactions is effec-
tively controlled. Formation of hot spots or hot zones a
known problem in the fixed bed reactors is prevented since
heat is transferred and distributed uniformly within the

15   liquid. The efficient temperature control is necessary to
reduce by-product formation as mentioned above and to mini-
mise deactivation of the catalyst.

SUMMARY OF THE INVENTION

20

The present innovation is a liquid phase process for the
production of methanol being carried out in a slurry-bed
reactor. In this process, methanol product is utilised as a
catalyst suspension liquid medium. This process exploits

25   the condensing conditions to produce methanol. The methanol
partial pressure (calculated from the gas phase equilibrium
constant) is larger than the boiling pressure of methanol
at the given temperature resulting in a condensation of the
methanol product. Synthesis gas conversion is thereby not

30   limited by equilibrium. The equilibrium and saturation com-
position is affected by temperature. For an increase in

temperature, the pressure needs to be increased to obtain
condensing conditions.

Accordingly, the invention is in its broadest aspect a pro-
cess for preparing methanol from a synthesis gas comprising
carbon monoxide, carbon dioxide and hydrogen by steps of:
(a) passing the synthesis gas into a reactor containing a
solid methanol conversion catalyst suspended in a liquid
phase of methanol and water;
(b) reacting the synthesis gas in presence of the suspended
catalyst at a pressure and temperature, where methanol be-
ing formed on the catalyst condenses into the liquid phase;
and
(c) withdrawing from the reactor a part of the liquid phase
containing formed methanol product.

Condensing conditions are defined as the operating condi-
tions of a methanol synthesis, wherein the methanol satura-
tion pressure is reached before the reaction equilibrium of
the synthesis gas composition is reached. The critical tem-
perature for methanol is 240°C. Non-condensing and condens-
ing conditions are separated for a given synthesis gas com-
position at a given operating temperature by a pressure,
P_{lim}. Above this pressure, condensing conditions are present
whereas below this pressure, non-condensing conditions are
present (see FIG.).

As the methanol saturation pressure increases with tempera-
ture and the equilibrium methanol pressure decreases with
temperature, P_{lim} increases with temperature. Above the
saturation curve, the total mole fraction of methanol in
the equilibrium mixture is depicted as a dashed line.

The characteristic of a preferred synthesis gas composition
is a low P_{lim}. The typical condensing conditions for pre-
ferred synthesis gas compositions is at temperatures 190-
240°C and at pressures 60-140 bar.

5

In one embodiment of the present invention, the synthesis
gas is compressed to a pressure higher than $P_{lim,t}$ and fed
to the slurry methanol reactor operated at a temperature,
t; the synthesis gas is converted in contact with a cata-
10   lyst active in methanol synthesis to a degree, where con-
densing conditions are obtained resulting in a directly
condensed methanol product and an effluent synthesis gas
saturated with methanol; the directly condensed methanol
product (primarily methanol, water and CO_2) constitutes the
15   suspension liquid medium for the catalyst active in metha-
nol synthesis; the effluent synthesis gas stream rich in
methanol is cooled down and separated to attain further
product retrieval. The directly condensed methanol product
used as suspension liquid is conventionally separated and
20   recovered from the solid catalyst particles e.g. by filtra-
tion. The solid catalyst particles are recycled to the
slurry reactor. The resulting methanol product is obtained
from both the directly condensed methanol product and the
retrieved methanol from the effluent synthesis gas.

25

In the known liquid phase methanol processes, the liquid
suspension medium is an inert hydrocarbon liquid and an ad-
ditional liquid phase is introduced into the system. This
additional liquid phase must be separated from the product
30   methanol. By the inventive methanol process, there is no
need for a liquid phase separation stage, since the product
and suspension liquid is the same component, i.e. methanol

and minor amounts of water. Hence, a high purity methanol product will be withdrawn from the reaction, and contamination of high molecular weight hydrocarbons can be avoided.

5   The liquid phase slurry reactor represents a solution to the heat removal problem in the known methanol process. The reactions for methanol formation from carbon monoxide and/or carbon dioxide are strongly exothermic. In gas phase reactors, the strong exothermic reaction creates a zone with high temperature of typical around 280°C or higher

10   within the catalyst tube, which promotes formation of by-products. The by-products formed are mainly higher alcohols such as ethanol, propanol, butanol, various esters and ketones. It is costly to separate these components from the

15   methanol product due to the formation of azeotropes between ketones, esters and methanol and ethanol and water. As a further disadvantage, the catalysts within the hot zones deactivate more rapidly. In the liquid phase reactor, the liquid phase reaction heat is absorbed in the liquid. The

20   temperature can be better controlled and no hot zones are formed. Hence the formation of by-products is kept at a minimum.

        Since heat removal is more efficient in the liquid phase

25   process, mixtures of a wide range of gas compositions can be treated. The main advantage of the invention is that a CO-rich synthesis gas can be treated. Synthesis gas mixture compositions in the range of 15-30 vol.% CO, 60-74 vol.% hydrogen and 0.5-15 vol.% carbon dioxide have been treated.

30   For a low content of carbon dioxide, the concentration of water in the methanol product will be low.

The process of the invention has the advantage of providing a high single-pass conversion. The high conversion is obtained because the conversion of methanol is not limited by thermodynamic equilibrium at condensing conditions as mentioned above.

By the process according to the invention a synthesis gas containing carbon dioxide can be processed. This is advantageous because it is expensive to produce a synthesis gas with low CO_2.

Cooling of the process can be performed by using cooling tubes producing medium or low-pressure steam. The tubes can be arranged in the methanol/water slurry and ensure that the temperature is kept at an almost constant level. Circulation of liquid around the tubes provides an improved temperature distribution and control. In a tubular fixed-bed reactor, hot zones are usually formed in the centre of the catalyst tube since the reaction is very exothermic. This promotes by-product formation as already discussed above.

Even an effective temperature control does, however, not prevent formation of some small amounts of by-products, including the aforementioned higher alcohols, ketones and ester compounds.

A main advantage of the process according to the invention is that by-products being formed during the methanol reaction may be recycled to the reactor and the reaction suspension, which by means of the chemical equilibrium between methanol and by-products being formed by reaction of methanol with reactants being present in the suspension prevents

net production of by-products as discussed in more detail below.

The produced raw methanol can be used either as fuel metha-
nol or fractionated into chemical grade methanol.

DETAILED DESCRIPTION OF THE INVENTION

By the invention methanol synthesis gas into a liquid
phase, which consists of catalyst suspended in methanol,
thereby reacting the synthesis gas to produce methanol. A
small fraction of water can be tolerated (0-3 vol.%) in the
methanol suspension without a significant deactivation of
the catalyst.

The process can be operated as a once-through process and
as a process in which unconverted gas is recycled.

The separation of the methanol product from the catalyst
may be accomplished by inserting filters within the reac-
tor. This will prevent the catalyst from leaving the reac-
tor. Other systems would include filtration of the product
or cyclone treatment outside the reactor.

The synthesis gas is low in carbon dioxide giving a product
with low water content. Results have shown that the water
production is around 0.02 g/g methanol.

The low water content confirms that the water gas shift re-
action is active and that most of the produced water is
consumed by this reaction.

The results also show that water can be tolerated in the present catalyst system. A water concentration of 0.55 wt% does not decrease the reaction rate to a high extent.

5   The methanol product after reaction at for example 202°C and 116 bar in a once-through process consists of small amounts of water (1.64 wt%), DME (0.19 wt%), methyl formate (0.92 wt%), ethanol (0.29 wt%), acetic acid methyl ester (0.09 wt%) and carbonic acid di-methyl ester (0.06 wt%). In

10   addition, traces of acetone, methane dimethoxy, 1-propanol, formic acid (2-methyl ethyl ester) and carbonic acid di-methyl ester may be found (< 0.03 wt%).

The present innovation provides means for keeping by-
15   product concentration such as methyl formate concentration at a constant level in the reactor. Methyl formate can be separated from the methanol product and recycled to the re-actor. By recycling a methyl-formate-rich stream to the re-actor, chemical equilibrium will be established in the re-
20   actor and there will be no net production of methyl for-mate. Example 7 illustrates the reduction of methyl formate in the liquid phase from 35 mol% to 5 mol% at 200°C and 132 bar. At these conditions reactions (10) and (11) are shifted towards methanol production

25

$$CH_3OH + CO = HCOOCH_3 \qquad (7)$$
$$HCOOCH_3 + 2H_2 = 2CH_3OH \qquad (8)$$
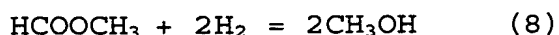
In this case an activated commercial catalyst available
30   from Haldor Topsøe A/S under the tradename MK-101P is used for methanol production. This is a Cu/Zn/Al-based catalyst.

A number of other catalysts for methanol production may
also be employed.

EXAMPLES

The following examples illustrate the results obtained with
a batch process system. The composition of the gases that
have been treated is given in Table 1.

Table 1

Synthesis gas composition

	Gas A [vol.%]	Gas B [vol.%]	Gas C [vol.%]	Gas D [vol.%]
H_2	60.	74.	60.	60.
CO	30.	25.5	25.	15.
CO_2	5.	0.5	5.	15.
N_2	5.	0.	10.	10.
Total	100.	100.	100.	100.
H_2/CO	2.0	3.0	2.4	4.
CO_2/CO	0.17	0.02	0.2	1.

Example 1

A 120 ml autoclave reactor was loaded with active catalyst
and methanol. Activated MK-101 (pulverised) is employed as
catalyst. The autoclave was connected to a gas reservoir
that contained a mixture of synthesis gas "A" comprising of
hydrogen (60 vol.%), nitrogen (5 vol.%), carbon monoxide
(30 vol.%) and carbon dioxide (5 vol.%) at 21°C and 162
bar. The volume of the gas reservoir was 0.5 ℓ. The process
was a closed batch system since neither gas nor liquid was
removed from the system until the reaction was completed.
The connection between the reactor and gas reservoir was
opened. The reaction occurred in the autoclave at a con-
stant pressure of 116 bar and a constant temperature of

202°C. The autoclave was agitated by stirring at 500 rpm. As the reaction proceeded, carbon dioxide and hydrogen were converted to methanol and water. The produced methanol and water condensed to liquid. Carbon monoxide reacted with water to produce hydrogen and carbon dioxide in the water gas shift reaction. The reactants were taken from the gas reservoir. The pressure drop in the gas reservoir was monitored and was used to determine the amount of gas consumed and hence the amount of methanol formed. With the pressure drop, the amount of methanol produced was calculated, assuming that reaction (7) resulted in the pressure drop. As the pressure in the gas reservoir had dropped to 121 bar, it was refilled to 162 bar and the reaction proceeded spontaneously until the gas reservoir pressure had dropped to 120 bar. Since the gas composition in the reactor changed with time, the reaction rate slowly decreased with time. A pressure drop corresponding to a gas consumption of 1.7 moles of synthesis gas resulted in 13.4 g of measured methanol product.

Table 2 illustrates the produced amount of methanol obtained for selected operating temperatures and pressures in the presented examples.

Example 2

Example 1 was repeated at a pressure of 109 bar and a temperature of 180°C, but with synthesis gas mixture "B" comprising of 74 vol.% hydrogen, 25.5 vol.% carbon monoxide and 0.5 vol.% carbon dioxide. A fresh catalyst suspension Pwas employed with activated catalyst. The gas was taken from the gas reservoir at 21.2°C and a pressure of 168.9 bar. Agitation was maintained at 500 rpm. Reaction contin-

ued spontaneously until a gas reservoir pressure of 130.6 bar. 6.3 g of methanol product was produced.

Example 3

Example 1 was repeated, at a pressure of 137 bar and a temperature of 200°C with the synthesis gas B from Example 2. The methanol suspension consisted of around 0.8 wt% of water originating from previous experiment. The same catalyst suspension was employed as in Example 2. The gas was taken from the reservoir at 170.4 bar at 21.6°C. The agitation rate was 500 rpm. At a reactor pressure of 131.4 bar, the reaction was terminated. The calculated product was 6.3 g.

Table 2

Conditions for methanol production

Gas	Pressure (bar)	Temperature (°C)	ΔP (bar)	MeOH (g)
A	116	202	83.0	13.4
B	109	180	38.3	6.3
B	137	200	38.9	6.3
C	137	210	47.6	7.8
D	109	180	40.0	6.8

Example 4

Example 1 was repeated, but at a pressure of 137 bar and a temperature of 210°C with synthesis gas mixture "C" comprising of 60 vol.% hydrogen, 10 vol.% nitrogen, 25 vol.% carbon monoxide and 5 vol.% carbon dioxide. The same suspension had been used for 5 previous experiments. The gas was taken from the gas reservoir at 21.2°C and a pressure of 168 bar. Agitation was maintained at 500 rpm. The gas reservoir pressure dropped to 138.4 bar and the reservoir

was refilled to 167 bar. Reaction continued spontaneously to a gas reservoir pressure of 149 bar. 7.8 g of methanol product was produced.

5   **Example 5**

Example 1 was repeated, but at a pressure of 109 bar and a temperature of 180°C with synthesis gas mixture "D" comprising of 60 vol.% hydrogen, 10 vol.% nitrogen, 15 vol.% carbon monoxide and 15 vol.% carbon dioxide. The catalyst

10   suspension had been used in previous experiments. The gas was taken from the gas reservoir at 21.3°C and a pressure of 162 bar. Agitation was maintained at 500 rpm. Reaction continued spontaneously until a reservoir pressure of 122 bar. 6.8 g of methanol was produced.

15

        Example 6

Influence of water concentration.

The influence of water concentration was investigated. The

20   results are listed in Table 3.

        (6a) Methanol solution of <0.05 wt% water

Fresh activated catalyst was employed in a methanol suspension of below 0.05 wt% water. The synthesis gas B was added

25   at the operating conditions of 138 bar and 200°C. The gas was taken from the gas reservoir at 19.5°C and a pressure of 167 bar. The pressure dropped to 137 bar in the reservoir. The reservoir was refilled twice to 166 bar. The pressure drop was 30.2, 21.4 and 4 bar, respectively, in

30   each period. 9.1 g of methanol was produced. The water concentration in methanol after the experiment was 0.48 wt%.

(6b) Methanol solution of 5 wt% water

Example 6a was repeated but at 139 bar and 200°C re-using
the same catalyst as used in Example 6a. Water was added to
an initial concentration of 5 wt% in methanol. The pressure

5   drop was in total 48.3 bar, and 7.9 g of methanol was pro-
duced. The water concentration in methanol after the ex-
periment was 3.6 wt%.

(6c) Methanol solution of 9 wt% water

10   Example 6a was repeated at 141 bar and 200°C re-using the
same catalyst as used in Examples 6a and 6b. Water was
added to an initial concentration of 9 wt% in methanol. The
pressure drop was in total 47.8 bar and 7.8 g of methanol
was produced. The water concentration after the experiment

15   was 7.6 wt%.

Table 3

Methanol production in presence of water for gas B

P(bar)	T(°C)	$[H_2O]$ wt%	ΔP (bar)	MeOH (g)
138	200	< 0.05	55.6	9.1
139	200	5	48.3	7.9
141	200	9	47.8	7.8

20

Example 7

Reduction of methyl formate concentration.

25   This example illustrates that the concentration of the
abundant by-product methyl formate can be reduced signifi-
cantly by chemical equilibrium between hydrogen, carbon
monoxide, methyl formate and methanol in reaction (7) and

(8). Hence, if a methyl-formate-rich stream is recycled to the reactor, there will be no net production of methyl formate in the reactor.

5   The experiment was run with an initial concentration of 34.8 mole% methyl formate in a methanol suspension. The experiment was carried out at 200°C and 132 bar using the same procedure as in·the examples above. At 132 bar and 200°C, reactions (1) and (2) are shifted towards methanol
10   production. Fresh, activated catalyst was employed. The hydrogen-rich synthesis gas B was used. The pressure drop in the reservoir was 29 bar. The final concentration of methyl formate was reduced to 5.4 mole% in the liquid phase. This corresponds to an analysed exit dry gas concentration of
15   hydrogen of around 24 mole%.

Table 4

Liquid concentration of MF and methanol
before and after experiment

20

Component	X_L [mole %] start	X_L [mole %] end
Methyl formate	34.8	5.4
Methanol	65.2	94.6